

(10)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 578 838 A1

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **92107331.8**(51) Int. Cl.⁵: **C08F 10/00, C08F 4/02,
C08F 4/642**(22) Date of filing: **29.04.92**(43) Date of publication of application:
19.01.94 Bulletin 94/03(64) Designated Contracting States:
**AT BE CH DE DK ES FR GB GR IT LI LU NL PT
SE**(71) Applicant: **HOECHST AKTIENGESELLSCHAFT
D-65926 Frankfurt(DE)**(72) Inventor: **Herrmann, Hans-Friedrich Dr.
Im Steinfeld 3
D-64291 Darmstadt(DE)
Inventor: Bachmann, Bernd Dr.
Kreuzheck 4
D-65817 Eppstein/Taunus(DE)
Inventor: Spaleck, Walter Dr.
Sulzbacher Strasse 63
D-65835 Liederbach(DE)**(94) **Olefin polymerization catalyst, process for its preparation, and its use.**

(97) A supported polymerization catalyst which is applicable in all polymerization processes is comprised of the reaction product of (A) a supported organoaluminum compound and (B) a metallocene catalyst component.

EP 0 578 838 A1

Olefin polymerization catalyst, process for its preparation, and its use.

The present invention relates to a supported (heterogeneous) catalyst which can advantageously be employed in the polymerization of olefins.

Processes are known for the preparation of polyolefins using homogeneous catalyst systems comprising a transition-metal component of the metallocene type and a cocatalyst component, an oligomeric aluminum compound of the aluminoxane type (usually methylaluminoxane ("MAO") which have high activity and give polymers or copolymers with a narrow molecular weight distribution (cf. EP-A-69 951).

A major disadvantage of these soluble metallocene/methylaluminoxane catalyst systems in processes where the polymer is formed as a solid is the formation of thick deposits on reactor walls and stirrers. These deposits are always formed due to agglomeration (Polymer Commun. 32 (1991) 58) of the polymer particles if the metallocene or the aluminoxane or both are used as a solution in the suspension medium. Deposits of this type in the reactor systems must be removed regularly since they rapidly reach considerable thicknesses, have high strength and prevent heat exchange with the cooling medium.

It has been attempted to support the catalyst by mixing MAO and metallocene with inorganic supports (EP 206 794). In order to improve the supporting, it has been proposed (WO 88/01626) to specially treat the support materials with adhesion promoters. Furthermore, it is known (EP 295 312) that the solubility of the methylaluminoxane used can be reduced, in a complex procedure, by means of non-polar solvents such as n-decane. However, these support methods are not completely effective and result, for example, in detachment of the aluminum or transition-metal components in a typical medium for suspension or solution polymerization.

As an alternative, it has been proposed to prepare methylaluminoxane by reacting water-containing SiO_2 with trimethylaluminum and to use the resultant suspension as a support for metallocenes (EP 323 716) or to carry out the entire reaction of trimethylaluminum, water-containing SiO_2 and metallocene in the polymerization reactor, in which the polymerization is subsequently carried out (EP 170 059). However, these processes firstly also give methylaluminoxanes dissolved in the reaction medium, which eliminate the advantage of the support, and secondly the supported aluminoxanes have significantly lower polymerization activity since only the overall stoichiometry is determined and the local control of the reaction stoichiometry of water and trimethylaluminum is inadequate.

The object was therefore to find a generally applicable way of fixing metallocene polymerization catalysts to supports which is simple and inexpensive to carry out and can be employed universally without significantly impairing the activity of the catalyst.

Surprisingly, a good and simple support method which is universally applicable in all polymerization processes arises if a supported organoaluminum catalyst component A is reacted with an organometallic, soluble catalyst component B. The use of the supported organoaluminum component A prevents any detachment of aluminum or transition-metal compounds under polymerization conditions.

The resultant catalyst system according to the invention does not require any additional cocatalyst for activation and completely prevents the formation of reactor deposits.

A further advantage of the catalyst system according to the invention is that aromatic solvents can be avoided completely, and consequently the resultant polymer product is not contaminated by traces of aromatic hydrocarbons. Such products are advantageous in applications in the foodstuffs and medical sectors.

To prepare the supported, organoaluminum compound (catalyst component A), the support is suspended in the solution of at least one alkylaluminum compound under inert conditions, and this suspension is hydrolyzed by means of the addition of water.

To prepare the supported, organoaluminum compound (catalyst component A), the support is suspended in the solution of at least one alkylaluminum compound under inert conditions, and this suspension is hydrolyzed by means of water. The support is an oxide of silicon or aluminum which may additionally contain one or more other oxides of the elements Al, K, Mg, Na, Si, Ti or Zr and whose surface may additionally be rendered hydrophobic by reaction with alkylsilanes, alkylhalosilanes, alkoxysilanes, silazanes, siloxanes or other alkyl compounds. Before use, the support can be freed from adsorbed water and oxygen in vacuo, in an oven, in a heated fluidized bed or in another way. The support pretreated in this way has a residual water content, which can be removed by igniting at 1000°C for 2 hours, of less than 3% by weight.

Inorganic supports which can be employed are oxides produced by flame pyrolysis by burning elemental halides, for example, chlorosilanes $\text{H}_n\text{SiCl}_{4-n}$, in an oxyhydrogen gas flame or those which can be prepared as silica gels in certain particle size distributions and particle shapes.

To prepare catalyst component A, the support described is metered into the solution of at least one alkylaluminum compound of the formula AlRR^1R^2 where the radicals R, R^1 and R^2 may be identical or

different and are a C₁-C₆-alkyl group, a C₁-C₆-fluoroalkyl group, a C₆-C₁₈-aryl group, a C₆-C₁₈-fluoroaryl group or hydrogen, preferably methyl, ethyl, i-propyl, i-butyl or n-butyl, under inert conditions and is suspended by stirring, pumping or in another way. The support is employed in an amount of less than 0.1 kg, preferably less than 0.05 kg, per mol of alkylaluminum, and the amount of solvent is selected so that a maximum of 20 % by weight, preferably a maximum of 10 % by weight, of support are suspended. Besides known aromatic solvents such as toluene, it is also possible to use aliphatic solvents such as pentane, hexane, heptane, n-decane or diesel oils (boiling points in the range 60-300 °C).

Water or solutions, mixtures or emulsions of water with other solvents are carefully added to the support suspension prepared in this way at temperatures of from -20 to +60 °C with cooling and intimate stirring or in a pumped circulation with considerable turbulence or in another way. The water may be metered in continuously or in small portions and the total amount of water is between 50 mol% and 100 mol%, preferably between 50 mol% and 80 mol%, based on the number of mols of aluminum of the initially introduced alkylaluminum compounds.

The catalyst component A prepared in this way can be washed as prepared as a suspension or by repeated decantation or separated off by filtration, washed and then resuspended or dried.

However, catalyst component A can also be prepared analogously to other MAO preparation processes if water is introduced in solid or liquid form and the pure alkylaluminum compound solution is replaced by a suspension of the support in an alkylaluminum compound solution. Processes of this type are described, for example, in DE 3731665 and DE 4004477.

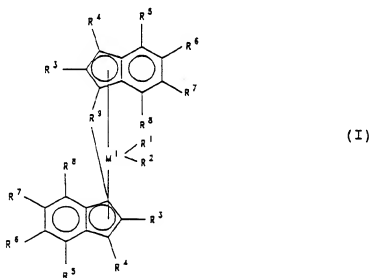
Catalyst component B is a metallocene or a mixture of more than one metallocene.

The catalysts obtained when more than one metallocene is employed are particularly suitable for the preparation of so-called reactor blends with bi- or multi-modal molecular weight distributions.

In principle, any metallocene can be employed, irrespective of the structure and composition. The metallocenes may be bridged or unbridged, and contain identical or different ligands. The metallocenes are compounds of metals from groups IVb, Vb or Vlb of the Periodic Table, for example compounds of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum or tungsten, preferably of zirconium, hafnium or titanium, in particular of zirconium.

Metallocenes of this type are known and are described, for example, in the following documents: EP-A-336 127, EP-A-336 128, EP-A-387 690, EP-A-387 691, EP-A-302 424, EP-A-129 368, EP-A-320 762, EP-A-284 707, EP-A-316 155, EP-A-351 392, US -5 017 714 and J. Organomet. Chem., 342 (1988) 21.

Of particular interest are metallocenes, specifically zirconocenes, which carry indenyl derivatives as ligands. These are preferably compounds of the formula I



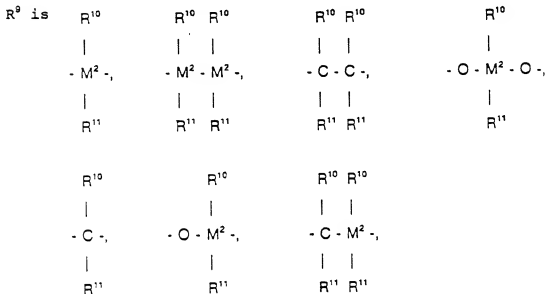
in which

M¹ is a metal from group IVb, Vb or Vlb of the Periodic Table,
 R¹ and R² are identical or different and are a hydrogen atom, a C₁-C₁₀-alkyl group, a C₁-C₁₀-alkoxy group, a C₆-C₁₀-aryl group, a C₆-C₁₀-aryloxy group, a C₂-C₁₀-alkenyl group, a C₇-C₁₀-aryllalkyl group, a C₇-C₁₀-alkylaryl group, a C₈-C₁₀-aryllalkenyl group, a OH group or a

halogen atom,

the radicals R^3 are identical or different and are a hydrogen atom, a halogen atom, a C_1 - C_{10} -alkyl group, which may be halogenated, a C_6 - C_{10} -aryl group, a $-NR_2$, $-SR$, $-OSiR_3$, $-SiR_3$ or PR_2 radical in which R is a halogen atom, a C_1 - C_{10} -alkyl group or a C_6 - C_{10} -aryl group,

R^4 to R^8 are as defined for R^3 or adjacent radicals R^4 to R^8 form an aromatic or aliphatic ring together with the atoms connecting them,



$=BR^{10}$, $=AlR^{10}$, $-Ge-$, $-Sn-$, $-O-$, $-S-$, $=SO$, $=SO_2$, $=NR^{10}$, $=CO$, $=PR^{10}$, $=P(O)R^{10}$ or hydrogen,

where

R^{10} and R^{11} are identical or different and are a hydrogen atom, a halogen atom, a C_1 - C_{10} -alkyl group, a C_1 - C_{10} -fluoroalkyl group, a C_6 - C_{10} -aryl group, a C_6 - C_{10} -fluoroaryl group, a C_1 - C_{10} -alkoxy group, a C_2 - C_{10} -alkenyl group, a C_7 - C_{10} -arylalkyl group, a C_6 - C_{10} -arylalkenyl group or a C_7 - C_{10} -alkylaryl group, or R^{10} and R^{11} , in each case together with the atoms connecting them, for a ring, and

M^2 is silicon, germanium or tin.

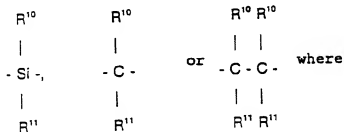
The 4,5,6,7-tetrahydroindeny analogs corresponding to the compounds I are likewise of importance.

In the formula I, it is preferred that M^1 is zirconium,

R^1 and R^2 are identical and are methyl or chlorine, in particular chlorine,

R^3 - R^8 are hydrogen or C_1 - C_4 -alkyl,

R^9 is



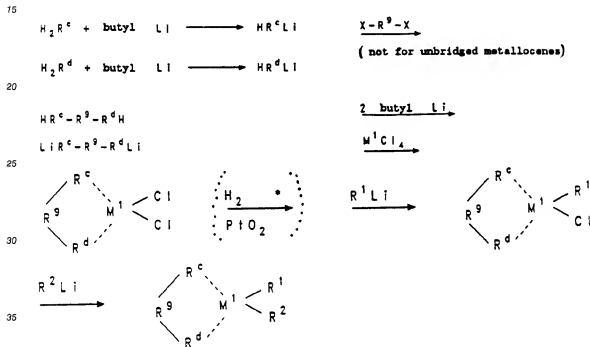
R^{10} and R^{11} are identical or different and are C_1 - C_4 -alkyl or C_6 - C_{10} -aryl. In particular, R^{10} and R^{11} are identical or different and are methyl or phenyl.

The indenyl or tetrahydroindenyl ligands of formula I are preferably substituted in 2-, 2,4-, 4,7-, 2,6-, 2,4,6-, 2,5,6-, 2,4,5,6- or 2,4,5,6,7-positions, in particular in 2,4,6-position, preferably by a C_1 - C_4 -alkyl group, such as, for example, methyl, ethyl or isopropyl. The 2-position is preferably substituted by methyl.

Also of particular importance are compounds I in which the substituents in the 4- and 5-positions of the indenyl radicals (R^3 and R^6), together with the atoms connecting them, form a benzene ring. This fused ring system may likewise be substituted by radicals as defined for R^3 - R^6 . An example of a compound I of this type is dimethylsilanediylbis(2-methyl-4,5-benzoidenyl)zirconium dichloride.

The metallocenes I are particularly suitable for the preparation of high-molecular weight polyolefins of high stereoregularity and high molecular weight.

The metallocenes I and the metallocenes described in the documents cited can be prepared, for example, in accordance with the reaction scheme below:



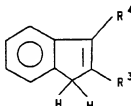
$X = Cl, Br, I$, or O-tosyl; H_2R^c and $H_2R^d \neq$ ligands, for example (substituted) indene

* additional hydrogenation step if, for example, indenyl ligands are to be converted into tetrahydroindenyl ligands.

The preparation processes are in principle known from the literature; cf. Journal of Organometallic Chem. 288 (1985) 63 - 67, EP-A-320 762 and the cited documents with respect to the metallocenes described therein.

The compounds I are prepared using variously substituted indenes as starting materials (H_2R^c and H_2R^d ; cf. the reaction scheme shown). Some of these indene derivatives are known and are commercially available. Specifically substituted indenes can be prepared by the processes indicated below:

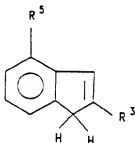
a) H_2R^c and $H_2R^d =$



The synthesis is carried out in accordance with or analogous to the references below:

J. Org. Chem., 49 (1984) 4226 - 4237; J. Chem. Soc., Perkin II, 1981, 403 - 408; J. Am. Chem. Soc., 106 (1984) 6702; J. Am. Chem. Soc., 65 (1943) 567; J. Med. Chem., 30 (1987) 1303 - 1308 and Chem. Ber. 85 (1952) 78 - 85.

b) H_2R^c and H_2R^d =



The 2,4-substituted indenenes H_2R^c and H_2R^d used as starting substances can be prepared by two different routes:

b1) The starting compound used is a ketoaldehyde of the formula shown in the reaction scheme below, whose preparation is known (Synthesis 1985, 1058).

The reaction of this ketoaldehyde with cyclopentadiene is carried out in an inert solvent in the presence of a base. Alcohols, such as methanol, ethanol or t-butanol, in particular methanol, are preferably used.

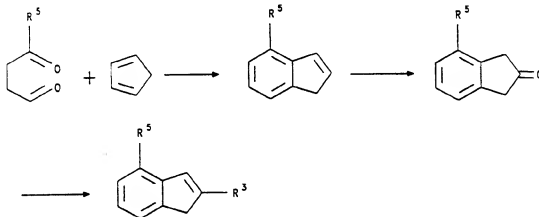
Bases which can be used are a large number of compounds. Examples which may be mentioned are alkali and alkaline earth metal hydroxides, alkali and alkaline earth metal alkoxides, such as sodium methoxide, sodium ethoxide and potassium tertiary butoxide, amides, such as lithium diisopropylamide or amines. Preference is given to sodium ethoxide, potassium tertiary butoxide and potassium hydroxide. The molar ratio between the starting compounds, including the bases used, can vary within broad limits. The ketoaldehyde : cyclopentadiene : base molar ratio is preferably 1 : 1 - 1.5 : 2-3, in particular 1 : 1.1 : 2.5.

The reaction temperature is preferably from -40 to 100 °C, in particular from 0 to 25 °C.

The reaction times generally vary between 10 minutes and 100 hours, preferably between 1 and 30 hours.

The substituent in the 2-position can be introduced by a Grignard reaction after conversion of the 4-monosubstituted indene into the 4-monosubstituted 2-indanone by a general procedure (Organic Synthesis, Coll. Vol. V, 1973, 647). The subsequent elimination of water gives the 2,4-substituted indenenes.

The 2,4-substituted indenenes are obtained as double bond isomers which can be employed directly for the synthesis of the corresponding metallocene complexes.



b2) Another possible and advantageous strategy involves the following scheme:

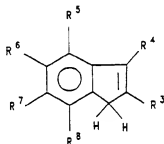
A 2-substituted benzyl halide is reacted with an appropriately substituted malonic diester analogously to a process known from the literature (J. Org. Chem. 1958, 23, 1437) to give the disubstituted malonic diester.

Hydrolysis of the diester and decarboxylation by conventional processes gives a disubstituted propionic acid derivative.

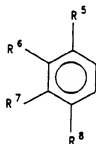
Ring closure to give the 2,4-disubstituted 1-indanone is carried out by customary processes (Friedel-Crafts reaction) after conversion of the carboxylic acid into the carboxylic acid chloride.

Reduction of the ketone by known methods and subsequent elimination of water gives the 2,4-disubstituted indenenes.

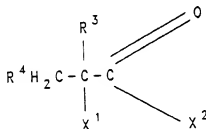
c) H_2R^c and H_2R^d =



The compounds H_2R^c and H_2R^d are prepared by reacting a compound II

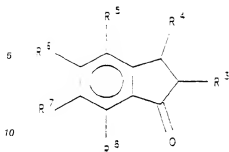


with a compound III

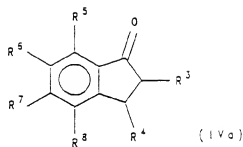


or the anhydride thereof in the presence of a Friedel-Crafts catalyst. In this formula, X^1 and X^2 are a nucleophilic leaving group, such as, for example, halogen, hydroxyl groups or tosyl groups, in particular bromine or chlorine.

The indanones IV or IVa

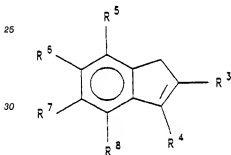


(IV)

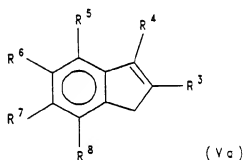


(IVa)

are obtained. Depending on the substitution pattern on the aromatic ring, the indanones can be obtained in the form of two constitutional isomers of the formulae IV and IVa. These can be reduced in pure form or as a mixture by methods known from the literature by means of reducing agents such as NaBH_4 or LiAlH_4 to the corresponding indanoles and subsequently dehydrated by means of acids, such as sulfuric acid, oxalic acid or p-toluene sulfonic acid, or alternatively by treatment with dehydrating substances, such as magnesium sulfate, sodium sulfate, aluminum oxide, silica gel or molecular sieves, to give indenenes of the formulae V and Va respectively ($\text{H}_2\text{R}^e/\text{H}_2\text{R}^d$) (Bull. Soc. Chim. Fr. 11 (1973) 3092; Organomet. 9 (1990) 3098).



(V)



(Va)

Examples of suitable Friedel-Crafts catalysts are AlCl_3 , AlBr_3 , FeCl_3 , SbCl_5 , SnCl_4 , BF_3 , TiCl_4 , ZnCl_2 , H_2SO_4 , polyphosphoric acid, H_3PO_4 or an $\text{AlCl}_3/\text{NaCl}$ melt, in particular AlCl_3 .

The starting compounds of the formulae II and III are known and are commercially available or can be prepared by processes known from the literature.

The reaction is carried out in an inert solvent, preferably methylene chloride or CS_2 . If the starting components are liquid, it is not necessary to use a solvent.

The molar ratios between the starting compounds, including the Friedel-Crafts catalyst, can vary within broad limits. The compound II : III : catalyst molar ratio is preferably 1 : 0.5 - 1.5 : 1 - 5, in particular 1 : 1 : 2.5 - 3.

The reaction temperature is preferably from 0 to 130°C , in particular from 25 to 80°C .

The reaction times generally vary between 30 minutes and 100 hours, preferably between 2 and 30 hours.

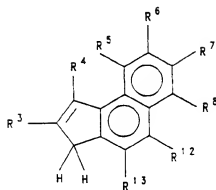
It is preferred to initially introduce a mixture of the compounds II and III and to meter in the Friedel-Crafts catalyst. The reverse sequence of addition is also possible.

The indanones of the formulae IV and IVa can be purified by distillation, column chromatography or crystallization.

The substituted indenenes may be obtained as double bond isomers (V/Va). These can be purified from byproducts by distillation, column chromatography or crystallization.

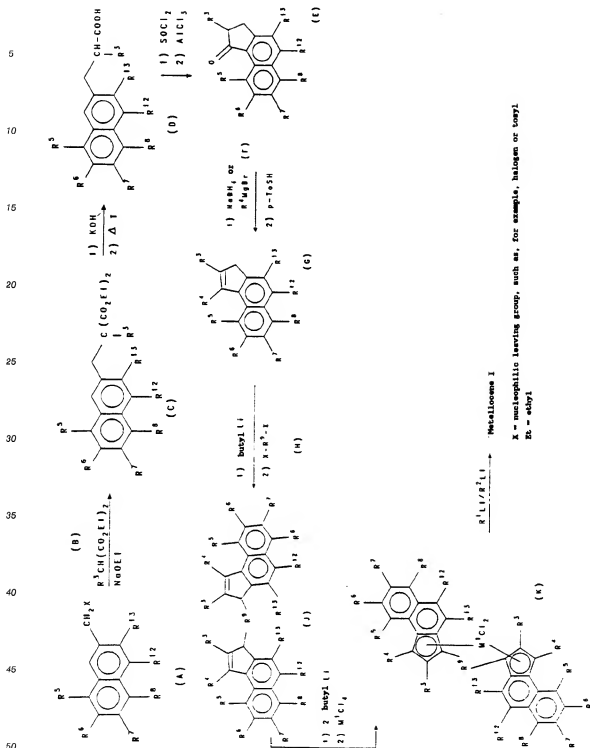
Starting from the indenenes of the formulae V and Va, which can be employed as an isomer mixture, the preparation of the metallocenes I proceeds by processes known from the literature (cf. AU-A-31 478/89, J. Organomet. Chem. 342 (1988) 21, and EP-A-284 707) in accordance with the reaction scheme shown.

d) H_2R^e and H_2R^d =



where R^{1,2} and R^{1,3} are as defined for R⁴ - R⁸

The preparation of these benzo-fused indenes and their further conversion to the metallocenes I are carried out in accordance with the reaction scheme below:



The naphthalene derivatives of the formula A are commercially available or can be prepared by methods known from the literature ("Friedel Crafts and Related Reactions", Wiley, New York, 1964, Vol. II, pp. 659-766, Bull. Soc. Chim. Belges, 58 (1949) 87, J. Amer. Chem. Soc. 89 (1967) 2411).

Conversion to the compounds of the formula C is carried out by methods known from the literature by reaction with substituted malonic esters of the formula B under basic conditions, such as, for example, in ethanolic solutions of sodium ethoxide (J. Org. Chem. 23 (1958) 1441, and J. Am. Chem. Soc. 70 (1948)

3569).

The compounds of the formula C are hydrolyzed by methods known from the literature using alkali metal hydroxides, such as potassium hydroxide or sodium hydroxide, and decarboxylated by methods known from the literature by thermolysis of the resultant dicarboxylic acid to give the compounds of the formula D (J. Org. Chem. 23 (1958) 1441, and J. Am. Chem. Soc. 70 (1948) 3569).

The ring closure to give the substituted benzoindanones of the formula E is carried out by methods known from the literature by reaction with chlorinating reagents, such as, for example, SOCl_2 , to give the corresponding acid chlorides and subsequent cyclization by means of a Friedel-Crafts catalyst in an inert solvent, such as, for example, by means of AlCl_3 or polyphosphoric acid in methylene chloride or CS_2 - (Organometallics 9 (1990) 3098, Bull. Soc. Chim. Fr. 3 (1967) 988, and J. Org. Chem. 49 (1984) 4226).

Conversion into the benzoindene derivatives of the formula G is carried out by methods known from the literature by reduction using sodium borohydride or lithium aluminum hydride in an inert solvent, such as, for example, diethyl ether or THF, or by alkylation using alkylating agents of the formula F or using alkyl lithium compounds to give the corresponding alcohols and dehydration of the alcohols under acidic conditions, such as, for example, using p-toluenesulfonic acid or oxalic acid, or by reaction with dehydrating substances, such as magnesium sulfate or molecular sieves (Organometallics 9 (1990) 3098, Acta. Chem. Scand. B 30 (1976) 527, and J. Amer. Chem. Soc. 65 (1943) 567).

The benzoindene derivatives of the formula G can also be synthesized in 4 steps by another synthetic route, not described in greater detail here, starting from substituted naphthalenes (Bull. Soc. Chim. Fr. 3 (1967) 988).

The preparation of the ligand systems of the formula J and the conversion to the bridged chiral metallocenes of the formula K and the isolation of the desired racemic form are known in principle (AU-A-31 478/89, J. Organomet. Chem. 342 (1988) 21, EP 0 284 707 and EP 0 320 762). To this end, the benzoindene derivative of the formula G is deprotonated by means of strong bases, such as, for example, butyllithium, in an inert solvent and reacted with a reagent of the formula H to give the ligand system of the formula J. This is subsequently deprotonated by means of two equivalents of a strong base, such as, for example, butyllithium, in an inert solvent and reacted with the corresponding metal tetrahalide, such as, for example, zirconium tetrachloride, in a suitable solvent. Suitable solvents are aliphatic and aromatic solvents, such as, for example, hexane or toluene, ethereal solvents, such as, for example, tetrahydrofuran or diethyl ether, or halogenated hydrocarbons, such as, for example, methylene chloride. The racemic and meso forms are separated by extraction or recrystallization using suitable solvents.

The derivitization to give the metallocenes of the formula I can be carried out by methods known from the literature, for example by reaction with alkylating agents, such as, for example, methyl lithium (Organometallics 9 (1990) 1539, J. Amer. Chem. Soc. 95 (1973) 6263, and EP 0 277 004).

The following compounds may be mentioned as examples of metallocenes which can be used according to the invention:

biscyclopentadienylzirconium dichloride,
biscyclopentadienylidimethylzirconium,
biscyclopentadienylidiphenylzirconium,
biscyclopentadienylidibenzylzirconium,
biscyclopentadienylbis(trimethylsilyl)zirconium,
bis(methylcyclopentadienyl)zirconium dichloride,
bis(1,2-dimethylcyclopentadienyl)zirconium dichloride,
bis(1,3-dimethylcyclopentadienyl)zirconium dichloride,
bis(1,2,4-trimethylcyclopentadienyl)zirconium dichloride,
bis(1,2,3-trimethylcyclopentadienyl)zirconium dichloride,
bis(pentamethylcyclopentadienyl)zirconium dichloride,
bis(indenyl)zirconium dichloride,
diphenylmethylene(9-fluorenyl)(cyclopentadienyl)zirconium dichloride,
dimethylsilyl(9-fluorenyl)(cyclopentadienyl)zirconium dichloride,
isopropylidene(9-fluorenyl)(cyclopentadienyl)zirconium dichloride,
dimethylsilylbis-1-tetrahydroindenylyl zirconium dichloride,
dimethylsilylbis-1-(2-methyltetrahydroindenylyl)zirconium dichloride,
dimethylsilylbis-1-(2,3,5-trimethylcyclopentadienyl)zirconium dichloride,
dimethylsilylbis-1-(2,4-dimethylcyclopentadienyl)zirconium dichloride,
dimethylsilylbis-1-indenylzirconium dichloride,
dimethylsilylbis-1-indenylidimethylzirconium,
dimethylgermylbis-1-indenylzirconium dichloride,

dimethylsilylbis-1-(2-methylindenyl)zirconium dichloride,
 dimethylsilylbis-1-(2-methyl-4-isopropylindenyl)zirconium dichloride,
 phenylmethylsilylbis-1-(2-methylindenyl)zirconium dichloride,
 dimethylsilylbis-1-(2-methyl-4-ethylindenyl)zirconium dichloride,
 5 ethylenebis-1-(4,7-dimethylindenyl)zirconium dichloride,
 phenyl(methyl)silylbis-1-indenylzirconium dichloride,
 phenyl(vinyl)silylbis-1-indenylzirconium dichloride,
 diphenylsilylbis-1-indenylzirconium dichloride,
 dimethylsilylbis(1-(2-methyl-4-t-butylindenyl))zirconium dichloride,
 10 methylphenylsilylbis(1-(2-methyl-4-isopropylindenyl))zirconium dichloride,
 dimethylsilylbis(1-(2-ethyl-4-methylindenyl))zirconium dichloride,
 dimethylsilylbis(1-(2,4-dimethylindenyl))zirconium dichloride,
 dimethylsilylbis(1-(2-methyl-4-ethylindenyl))dimethylzirconium,
 dimethylsilylbis(2-methyl-4,6-diisopropylindenyl)zirconium dichloride,
 15 dimethylsilylbis(2,4,6-trimethylindenyl)zirconium dichloride,
 methylphenylsilylbis(2-methyl-4,6-diisopropylindenyl)zirconium dichloride,
 1,2-ethanediybis(2-methyl-4,6-diisopropylindenyl)zirconium dichloride
 and dimethylsilylbis(2-methyl-4,5-benzoidenyl)zirconium dichloride.

Chiral metallocenes are preferably employed as a racemate in the preparation of the catalyst according
 20 to the invention. However, it is also possible to use the pure R- or S-form. Optically active polymer can be
 prepared using these pure stereoisomeric forms. However, the meso form of the metallocenes should be
 separated off since the polymerization-active center (the metal atom) in these compounds is no longer chiral
 due to mirror symmetry at the central metal and it is therefore not possible to produce any highly tactic
 polymer. If the meso form is not separated off, atactic polymer is formed alongside isotactic and
 25 syndiotactic polymer. For certain applications, for example soft moldings, or for the production of polyethy-
 ene grades, this may be entirely desirable.

The supported catalyst is prepared at a temperature between -20 and +120 °C, preferably at from 15 to
 40 °C, by reacting the catalyst component A with the catalyst component B in such a manner that the
 insoluble catalyst component A is reacted as a 1-40% by weight, preferably 5-20% by weight, suspension
 30 in an aliphatic, inert suspension medium, such as n-decane, hexane, heptane or diesel oil, with a solution in
 an inert solvent, such as toluene, hexane, heptane or dichloromethane, or with the finely ground solid of
 catalyst component B. Conversely, it is also possible to react a solution of catalyst component B with the
 solid of catalyst component A.

The reaction is carried out by vigorous mixing, for example by stirring at an Al/Zr molar ratio of between
 35 100/1 and 10,000/1, preferably between 100/1 and 2,000/1, and a reaction time of between 5 and 120
 minutes, preferably between 10 and 30 minutes, under inert conditions.

During the reaction time for the preparation of the catalyst, changes in the color of the reaction mixture
 occur, in particular if metallocenes having absorption maxima in the visible region are used; the progress of
 the reaction can be followed from these changes in color.

40 When the reaction time is complete, the supernatant solution is separated off, for example by filtration
 or decanting, and the solid which remains is washed once to 5 times with an inert suspending medium,
 such as toluene, n-decane, hexane, diesel oil or dichloromethane. This washing operation (extraction) serves
 to remove soluble constituents in the catalyst formed, in particular to remove unreacted and thus soluble
 metallocene. It is advantageous, but not necessary, to carry out the entire reaction in a pressure filter. It is
 45 also possible to use various inert solvents for washing the solid. The filtrate and the washing liquids are
 colorless, irrespective of the metallocene employed previously.

The catalyst prepared in this way can be dried in vacuo as a powder or resuspended as a suspension,
 in an inert suspending medium, such as, for example, heptane, hexane, diesel oil or dichloromethane,
 50 metered into the polymerization system.

The present invention furthermore relates to a process for the preparation of an olefin polymer by
 polymerization or copolymerization of an olefin of the formula $R^a-CH=CH-R^b$ in which R^a and R^b are
 identical or different and are a hydrogen atom or a hydrocarbon radical having 1 to 14 carbon atoms, or R^a
 and R^b , together with the atoms connecting them, can form a ring, at a temperature of from -60 to 200 °C,
 at a pressure of from 0.5 to 100 bar, in solution, in suspension or in the gas phase, in the presence of a
 55 catalyst, when the catalyst used is the reaction product according to the invention.

The polymerization or copolymerization is carried out in a known manner in solution, in suspension or in
 the gas phase, continuously or batchwise, in one or more steps, at a temperature of from -60 to 200 °C,
 preferably from 30 to 80 °C, particularly preferably from 50 to 80 °C. Olefins of the formula $R^a-CH=CH-R^b$

are polymerized or copolymerized. In this formula, R^a and R^b are identical or different and are a hydrogen atom or a alkyl radical having 1 to 14 carbon atoms. However, R^a and R^b may also, together with the carbon atoms connecting them, form a ring. Examples of such olefins are ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, norbornene, norbornadiene and 1,4,5,8-dimethano-1,2,3,4, 4a,5,8,8a-octahydronaphthalene (DMON). In particular, propylene and ethylene are polymerized or copolymerized.

If necessary, hydrogen is added as molecular weight regulator and/or to increase the activity. The total pressure in the polymerization system is from 0.5 to 100 bar. The polymerization is preferably carried out in the industrially particularly interesting pressure range of from 5 to 64 bar.

The catalyst according to the invention is preferably used in a concentration, based on the transition metal, of from 10^{-3} to 10^{-8} mol, preferably from 10^{-4} to 10^{-7} mol, of transition metal per dm^3 of solvent or per dm^3 of reactor volume.

If the polymerization is carried out as a suspension or solution polymerization, an inert solvent which is customary for the Ziegler low-pressure process is used. For example, the process is carried out in an aliphatic or cycloaliphatic hydrocarbon; specific examples of these are butane, pentane, hexane, heptane, isooctane, cyclohexane and methylcyclohexane.

It is furthermore possible to use a gasoline or hydrogenated diesel oil fraction. Toluene can also be used.

If inert solvents are used, the monomers are metered in in gas or liquid form.

The polymerization can last as long as desired, since the catalyst system to be used according to the invention only exhibits a slight time-dependent decrease in polymerization activity.

Before the catalyst is introduced into the reactor, another alkylaluminum compound, such as, for example, trimethylaluminum, triethylaluminum, triisobutylaluminum or isoprenylaluminum, can additionally be added to the polymerization system in a concentration of from 2 to 0.001 mmol of Al per kg of reactor contents in order to render the polymerization system inert (for example to remove catalyst poisons present in the olefin). However, it is not absolutely necessary to employ further substances to catalyze the polymerization reaction, i.e. the catalyst according to the invention can, and this is preferred, be used as the only catalyst for the olefin polymerization.

The molecular weight of the polymer formed can also be influenced by changing the polymerization temperature, periodic changes or a multistep process or the use of more than one metallocene also allowing polymers having a broad molecular weight distribution to be obtained.

In additions, the polymer molecular weight achieved using the solid catalyst according to the invention is determined by the type of metallocene used, by the aluminum compound and by the molar aluminum to metallocene ratio.

The process according to the invention (the catalyst according to the invention) is primarily distinguished by the fact that the undesired reactor deposits are prevented during the polymerization. A further advantage of the process is the complete omission of aromatic solvents and the simple way in which the catalyst is prepared.

By the process according to the invention, polymers with very narrow molecular weight distributions (M_w/M_n) of about 2 to 10, especially 2 to 4 can be obtained.

Examples:

All glass equipment was heated in vacuo and flushed with argon. All operations were carried out in Schlenk flasks with exclusion of moisture and oxygen. The solvents used were in each case freshly distilled over Na/K alloy under argon and stored in Schlenk flasks.

The polymer melting points indicated are determined by a DSC measurement for the 2nd melting (heating rate: $10^\circ/\text{min}$).

To prepare the catalyst component A, an explosion-proof stainless steel reactor was constructed with a 60 bar pumping system, inert gas supply, temperature control system via jacket cooling and a 2nd cooling circuit via a heat exchanger on the pumping system. The pumping system draws the reactor contents in by means of a pump via a connection on the reactor base, forces them into a mixer and back into the reactor through a rising line via a heat exchanger. The mixer is designed so that, due to a narrowed tube cross section, an increased flow rate is generated in the feed, in the turbulence zone of which a thin feed line is arranged axially and opposite to the flow direction, through which a defined amount of water can in each case be fed in cycles by means of 40 bar of argon. The reaction is monitored via a sampler on the pump circuit.

However, other reactors, as described, for example, in DE 37 31 665 and DE 40 04 477, are also suitable in principle.

The metallocene rac-dimethylsilylbis-1-(2-methylindenyl)zirconium dichloride is synthesized as described in DE-A 40 35 883 and DE-A 40 35 886. The metallocene diphenylmethylene-9-fluorenylcyclopentadienylzirconium dichloride is synthesized as described in EP 387 690. The metallocene isopropylidene-9-fluorenylcyclopentadienylzirconium dichloride is synthesized as described in J. Am. Chem. Soc., 110 (1988) 6255. The metallocene racdimethylsilylbis-1-(2-methyl-4,5-benzoindenyl)zirconium dichloride is synthesized as previously described herein (see Formula(K)).

The aluminum is determined after hydrolysis using water and sulfuric acid by complexometric titration by the Schwarzenbach method. Trimethylaluminum is purchased as a pure substance from SCHERING AG. Toluene-soluble methylaluminoxane is purchased for the comparative examples as a 10 % by weight toluene solution from SCHERING AG and, according to an aluminum determination, contains 36 mg of Al/mg. The mean degree of oligomerization, determined from the freezing point depression in benzene, is $n = 20$.

Example 1:

Preparation of catalyst component A:

5 dm³ of aromatic-free diesel oil (boiling point 100-120 °C) are introduced into a stirred 16 dm³ reactor under inert conditions, 0.50 dm³ of trimethylaluminum (5.2 mol) are added, and the temperature is held at 25 °C. 200g of Aerosil (R) 812 (Degussa AG) which has been previously dried at 120 °C in an argon fluidized bed are metered into this reactor via a solids hopper and homogeneously suspended with the aid of the stirrer and the pumping system. A total of 76.5 g of water in 0.1 ml portions at 15 second intervals are metered in at the mixer over the course of 3.25 hours. The pressure, raised by introduced argon and reaction gases, is kept constant at 10 bar by a pressure-release valve. When all the water has been added, the pumping system is switched off and stirring is continued for a further 5 hours at 25 °C.

The solid catalyst component A prepared in this way is employed as 12% strength by weight suspension in diesel oil (boiling point 100-120 °C). The aluminum content is 1.06 mmol of Al per ml of suspension. The isolated solid contains 31% by weight of Al. The suspension medium contains less than 0.1% by weight of aluminum.

Example 2:

5 ml of the suspension of catalyst component A from Example 1 are introduced into a G3 Schlenk frit under argon and filtered. The solid which remains is resuspended in 20 ml of an aromatic-free, inert diesel oil (boiling point 100 to 120 °C). 0.5 ml of a 1/500 molar solution of biscyclopentadienylzirconium dichloride in absolute toluene is metered into this suspension, and the mixture is stirred for 1/4 hour at 30 °C. The mixture is subsequently filtered, and the solid which remains is washed with 20 ml of diesel oil and resuspended in 20 ml of diesel oil for the polymerization.

Polymerization:

A dry 1.5 dm³ tubular reactor is flushed with nitrogen in order to remove the oxygen and filled with 0.9 dm³ of an inert diesel oil (boiling point 100-120 °C). After the reactor has been flushed with ethylene, the temperature is held at 70 °C, and the catalyst suspension is metered in at an ethylene pressure of 7 bar without introduction of additional activator. After 2 hours, the pressure in the reactor is released, and the polymer is filtered off from the suspension and dried for 12 hours in a vacuum drying cabinet. 23 g of polyethylene powder having a bulk density of 0.175 kg/dm³ and a viscosity of 392 cm³/g are obtained. The reactor exhibits no deposits on the outer wall or stirrer. The molecular weight distribution (according to GPC) is Mw/Mn = 2.6.

Comparative Example 1:

The polymerization from Example 2 is repeated, with the difference that the catalyst used is 0.029 mg of biscyclopentadienylzirconium dichloride dissolved in a 10% strength by weight solution of methylaluminoxane in toluene (12 mmol of Al). Under otherwise identical conditions, 40 g of polyethylene having a viscosity of 380 cm³/g and a bulk density of 0.060 kg/dm³ are produced. When the reactor is opened, a continuous deposit with a thickness of 1 mm is visible on the outer wall and stirrer.

Comparative Example 2:

The polymerization from Example 2 is repeated, with the difference that the mixture of 20 ml of the suspension of catalyst component A from Example 1 with 0.5 ml of a 1/500 molar solution of bis(cyclopentadienyl)zirconium dichloride in toluene is used without filtration and washing. Under otherwise identical conditions, 37.3 g of polyethylene having a viscosity of 407 cm³/g and a bulk density of 0.067 kg/dm³ are produced. When the reactor is opened, a continuous deposit with a thickness of 0.2 mm is visible on the outer wall and stirrer.

10 Example 3:

The catalyst preparation from Example 2 is repeated, with the difference that 800 ml of the suspension of catalyst component A from Example 1 and 11.7 mg of bis(cyclopentadienyl)zirconium dichloride, dissolved in toluene, are employed. A 160 dm³ reactor which has been rendered inert is filled with 80 l of diesel oil (boiling point 100-120 °C) and heated to 50 °C, and 3 bar of ethylene are introduced. The catalyst is added via a transfer tube, and the ethylene pressure is increased to 7 bar and the temperature is kept constant at 70 °C by cooling. After a polymerization time of 3 hours, the pressure in the reactor is released and the suspension is filtered off in a pressure filter. Drying in a vacuum drying cabinet gives 4.3 kg of polyethylene, corresponding to a reduced contact time yield of 5.1 [kg/(mmol·h·bar)], having a bulk density of 140 g/dm³. The reactor exhibits no deposits on the wall or stirrer. The product has a density of 0.953 g/cm³, a viscosity of 463 cm³/g and a molecular weight distribution (according to GPC) of $M_w/M_n = 2.5$.

Example 4:

The catalyst preparation from Example 2 is repeated, with the difference that the washing is carried out with anhydrous hexane instead of with diesel oil (boiling point 100-120 °C). The catalyst is subsequently dried for 2 hours at 10⁻³ mbar and 30 °C to give a free-flowing powder. Analysis shows 27% by weight of Al and 40 ppm of Zr.

1250 mg of the dry catalyst are mixed with 80 g of polystyrene powder which has been rendered inert, as a stirring aid, and the polymerization is carried out in a 1.5 dm³ reactor with propeller stirrer for 1 hour at 70 °C and at 4 bar of ethylene. The pressure in the reactor is released, and the powder is removed and extracted with boiling toluene. After drying in vacuo, 29 g of a polyethylene having a viscosity of 420 cm³/g remain.

35 Example 5:

30 mg of diphenylmethylen-9-fluorenylcyclopentadienylzirconium dichloride are dissolved in a little toluene and mixed with 60 ml of the suspension of catalyst component A from Example 1 in a Schlenk frit. After 15 minutes, the solution is filtered, and the filter cake is washed with diesel oil and subsequently resuspended in 20 ml of diesel oil.

Polymerization:

A dry nitrogen-flushed 16 dm³ reactor is filled with 10 dm³ of propylene and warmed to 30 °C. After 15 minutes, the catalyst suspension is metered into the reactor via a pressure lock without further addition of activator. On initiation of the polymerization, the internal reactor temperature is increased to the polymerization temperature of 50 °C at 10 °/min by additional supply of heat and is subsequently kept at this temperature by cooling. After a polymerization time of 1 hour, the polymerization is terminated by addition of isopropanol, the pressure in the reactor is released and the reactor is opened. The reactor wall and stirrer are completely free from deposits. Vacuum drying of the product gives 0.56 kg of free-flowing polypropylene powder having a viscosity of 350 cm³/g and a melting point (DSC) of 111.2 °C. The mean particle diameter d_{50} according to screen analysis is 800 µm.

Comparative Example 3:

To prepare the catalyst, 9.4 mg of diphenylmethylen-9-fluorenylcyclopentadienylzirconium dichloride are dissolved in 20 cm³ of a toluene solution of methylaluminoxane (corresponding to 27 mmol of Al) and reacted with the methylaluminoxane by standing for 15 minutes. In parallel, a dry 16 dm³ reactor is flushed

with nitrogen and filled with 10 dm³ of liquid propene. 30 cm³ of a toluene solution of methylaluminoxane are added to this reactor, and the mixture is stirred at 30 °C for 15 minutes. The catalyst solution is subsequently introduced into the reactor, and the polymerization system is heated to the polymerization temperature of 50 °C (10 °C/min) by supply of heat and kept at this temperature for 1 hour by cooling. The polymerization is then terminated by addition of 5 ml of isopropanol, the pressure in the reactor is released, and the reactor is opened. A continuous deposit with a thickness of 2 mm is evident. Vacuum drying of the product gives 0.2 kg of syndiotactic polypropylene having a viscosity of 502 cm³/g, $M_w = 4.97 \cdot 10^6$ g/mol, $M_w/M_n = 2.2$ and a melting point (DSC) of 134.1 °C. The mean particle diameter d_{50} according to screen analysis is 2500 µm.

Example 6:

The polymerization is carried out as in Example 5, with the difference that 4.9 mg of rac-dimethylsilylbis-2-methyl-1-indenylzirconium dichloride are reacted with 60 ml of a suspension of catalyst component A from Example 1 and the polymerization is carried out at 70 °C. After opening, the reactor is free from deposits. Vacuum drying of the product gives 0.35 kg of polymer having a viscosity of 170 cm³/g and a melting point (DSC) of 142.8 °C. The mean particle diameter d_{50} of the free-flowing powder according to screen analysis is 1000 µm, and the fines content (<100 µm) is 0.8% by weight.

Comparative Example 4:

The procedure is as in Comparative Example 3, with the difference that 5.2 mg of rac-dimethylsilylbis-1-(2-methylindenyl)zirconiumdichloride are employed and the polymerization is carried out at 70 °C.

After the polymerization, a continuous deposit with a thickness of 3 mm is evident. Vacuum drying of the product gives 1.3 kg of polypropylene having a viscosity of 151 cm³/g and a melting point (DSC) of 145 °C. The mean particle diameter d_{50} according to screen analysis is 350 µm.

Example 7:

1 mg of isopropylidene-9-fluorenylcyclopentadienylzirconium dichloride, dissolved in toluene, is added to 40 ml of a suspension of the solid catalyst component A from Example 1, and the mixture is stirred for 30 minutes. In parallel, a 1.5 l reactor is flushed with ethylene and filled with 600 cm³ of an 85% strength by weight solution of norbornene in toluene and 20 ml of a suspension of solid catalyst component A from Example 1, the mixture is subsequently stirred at 70 °C for 30 minutes and saturated with 6 bar of ethylene. After addition of the catalyst, the mixture is polymerized for 1 hour at 70 °C, the pressure being kept constant at 6 bar by subsequent introduction of ethylene. The reaction solution is decompressed, stirred for 30 minutes with 10 cm³ of water and filtered. The clear solution is added dropwise to 5 dm³ of acetone, the mixture is stirred for 10 minutes, and the precipitated polymer is filtered off and washed with acetone. Drying at 80 °C in a vacuum drying cabinet gives 32 g of copolymer having a viscosity of 230 cm³/g and a glass transition temperature T_g of 156 °C.

comparative Example 5:

The polymerization from Example 7 is repeated, with the difference that the 40 cm³ of the suspension of the solid catalyst component A from Example 1 are replaced by 20 cm³ of a 10% strength by weight solution of MAO in toluene. 15.7 g of copolymer having a viscosity of 86 cm³/g and a glass transition temperature T_g of 156 °C are obtained.

Example 8:

The polymerization from Example 7 is repeated, with the difference that, instead of 1 mg of isopropylidene-9-fluorenylcyclopentadienylzirconium dichloride, 5 mg of diphenylmethylene-9-fluorenylcyclopentadienylzirconium dichloride are stirred with catalyst component A from Example 1 and the polymerization is carried out at 3 bar of ethylene and at 40 °C. 24 g of copolymer having a viscosity of 367 cm³/g and a glass transition temperature T_g of 176 °C are obtained.

Comparative Example 6:

The polymerization from Example 8 is repeated, with the difference that the 40 cm³ of suspension of the solid catalyst component A from Example 1 are replaced by 20 cm³ of a 10% strength by weight solution of MAO in toluene. 8.9 g of copolymer having a viscosity of 187 cm³/g are obtained.

Example 9:

Preparation of Catalyst component A:

The reaction from Example 1 is repeated, with the difference that the diesel oil is replaced by 6 dm³ of n-decane and the 200 g of Aerosil R 812 (Degussa AG) are replaced by 200 g of silica gel SD 3216-30 (GRACE AG). The silica gel has previously been dried for 10 hours at 140 °C in a heated fluidized bed. The BET surface area of this support is 310 m²/g. 72 g of water are metered into the resultant suspension in the same way.

The solid catalyst component A prepared in this way is employed as a 10% strength by weight suspension in n-decane. The aluminum content is 0.96 mmol of Al per ml of suspension. The isolated solid contains 28% by weight of Al. The suspension medium contains 0.1% by weight of aluminum.

Example 10:

40 ml of the suspension of the solid catalyst component A from Example 9 are filtered off with suction in a Schlenk frit and resuspended in diesel oil (boiling point 100-120 °C). 1.9 mg of rac-dimethylsilylbis(2-methyl-4,5-benzoinde-nyl)zirconium dichloride are dissolved in 5 ml of toluene, the solution is mixed with the suspension, and the mixture is filtered after 15 minutes. The filter cake is subsequently washed with a little diesel oil and resuspended in 5 ml of diesel oil.

Polymerization:

The polymerization is carried out as in Example 5. However, addition of the catalyst suspension is preceded by the metering of 15 ml of a 20% strength by weight solution of triisobutylaluminum in diesel oil into the reactor. Vacuum drying of the product gives 0.27 kg of free-flowing polypropylene powder having a viscosity of 380 cm³/g. The mean particle diameter d₅₀ according to screen analysis is 550 µm.

Example 11:

40 ml of the suspension of the solid catalyst component A from Example 9 are filtered with suction in a Schlenk frit and resuspended in diesel oil (boiling point 100-120 °C). 20.3 mg of rac-dimethylsilylbis(2-methylindenyl)zirconium dichloride are dissolved in 10 ml of toluene, the solution is mixed with the suspension, and the mixture is filtered after 15 minutes. The filter cake is subsequently washed with a little diesel oil and resuspended in 10 ml of diesel oil.

Polymerization:

A dry nitrogen-flushed 70 dm³ reactor is filled with 40 dm³ of propylene and warmed to 30 °C, and 60 ml of a 20% by weight solution of triisobutylaluminum in diesel oil are added. After 15 minutes, the catalyst suspension is metered in via a pressure lock. The internal temperature of the reactor is increased to 70 °C at 2 °C/min and subsequently kept at this temperature for 2 hours by cooling. The reaction is terminated by addition of isopropanol. The product suspension is decompressed, the pressure is released and the product is vacuum-dried to give 8.2 kg of free-flowing polypropylene powder having a viscosity of 160 cm³/g. The mean particle diameter d₅₀ is 550 µm, and the fines content (<100 µm) according to screen analysis is 1.5% by weight.

Example 12

6.2 ml of the suspension of the catalyst component A from Example 9 are introduced into a G3 Schlenk frit under argon and filtered. The solid which remains is resuspended in 20 ml of an aromatic-free, inert diesel oil (boiling point 100 to 120 °C). 0.25 ml of a 1/500 molar solution of bis(cyclopentadienyl)zirconium

dichloride in absolute toluene is metered into this suspension, and the mixture is stirred at 30 °C for 1/4 hour. The mixture is subsequently filtered, and the solid which remains is washed with 20 ml of diesel oil and resuspended in 20 ml of diesel oil for the polymerization.

5 Polymerization:

The polymerization is carried out as described in Example 2. 19 g of polyethylene powder having a bulk density of 0.160 kg/dm³ and a viscosity of 365 cm³/g are obtained. The reactor exhibits no deposits on the wall or stirrer. The molecular weight distribution (according to GPC) is $M_w/M_n = 2.6$.

10

Claims

1. A supported polymerization catalyst comprising the reaction product of (A) a supported, organoaluminum compound and (B) a metallocene catalyst component.

15

2. The polymerization catalyst according to Claim 1, wherein the supported, organoaluminum compound (A) is prepared by preparing a suspension of a support in a solution of at least one alkylaluminum compound under inert conditions and hydrolyzing the suspension by the addition of water to the suspension.

20

3. The polymerization catalyst according to Claim 2, wherein the alkylaluminum compound is of the formula $AlRR^1R^2$ where R, R¹ and R² may be identical or different and are a C₁-C₆-alkyl group, a C₁-C₆-fluoroalkyl group, a C₆-C₁₈-aryl group, a C₆-C₁₈-fluoroaryl group or hydrogen, preferably methyl, ethyl, i-propyl, i-butyl or n-butyl.

25

4. The polymerisation catalyst according to Claim 2 or 3, wherein the alkylaluminum compound is trimethylaluminum.

30

5. The polymerization catalyst according to one or more of Claims 2 - 4, wherein the support is an oxide of silicon or aluminum.

6. The polymerization catalyst according to one or more of Claims 2 - 5, wherein the support is employed in an amount of less than 0.1 kg per mol of alkylaluminum.

35

7. The polymerization catalyst according to one or more of Claims 1 - 6, wherein the metallocene catalyst component (B) is a metallocene or a mixture of more than one metallocene.

8. The polymerisation catalyst according to one or more of Claims 1 - 7, wherein the metallocene catalyst component (B) is a zirconocene.

40

9. A process for preparing the polymerization catalyst according to one or more of Claims 1 - 8, wherein (A) a supported, organoaluminum compound is reacted with (B) a metallocene catalyst component.

45

10. A process for the preparation of an olefin polymer by polymerization or copolymerization of an olefin of the formula $R^a-CH=CH-R^b$ in which R^a and R^b are identical or different and are a hydrogen atom or hydrocarbon radical having 1 to 14 carbon atoms, or R^a and R^b, together with the atoms connecting them, can form a ring, at a temperature of from -60 to 200 °C, at a pressure of from 0.5 to 100 bar, in solution, in suspension or in the gas phase, in the presence of a polymerisation catalyst, wherein the polymerization catalyst according to one or more of Claims 1 - 8 is used.

50

11. The process according to Claim 10, wherein ethylene or propylene is polymerized or copolymerized.

Claims for the following Contracting State : ES

55

1. A process for preparing a supported polymerization catalyst wherein (A) a supported, organoaluminum compound is reacted with (B) a metallocene catalyst component.

2. The process according to claim 1, wherein the supported, organoaluminum compound (A) is prepared by preparing a suspension of a support in a solution of at least one alkylaluminum compound under inert conditions and hydrolyzing the suspension by the addition of water to the suspension.
- 5 3. The process according to Claim 2, wherein the alkylaluminum compound is of the formula AlR^1R^2 where R^1 , R^2 and R^3 may be identical or different and are a C_1 - C_6 -alkyl group, a C_1 - C_6 -fluoroalkyl group, a C_6 - C_{18} -aryl group, a C_6 - C_{18} -fluoroaryl group or hydrogen, preferably methyl, ethyl, i-propyl, i-butyl or n-butyl.
- 10 4. The process according to Claim 2 or 3, wherein the alkylaluminum compound is trimethylaluminum.
5. The process according to one or more of Claims 2 - 4, wherein the support is an oxide of silicon or aluminum.
- 15 6. The process according to one or more of Claims 2 - 5, wherein the support is employed in an amount of less than 0.1 kg per mol of alkylaluminum.
7. The process according to one or more of Claims 1 - 6, wherein the metallocene catalyst component (B) is a metallocene or a mixture of more than one metallocene.
- 20 8. The process according to one or more of Claims 1 - 7, wherein the metallocene catalyst component (B) is a zirconocene.
9. A process for the preparation of an olefin polymer by polymerization or copolymerization of an olefin of the formula $R^a-CH=CH-R^b$ in which R^a and R^b are identical or different and are a hydrogen atom or hydrocarbon radical having 1 to 14 carbon atoms, or R^a and R^b , together with the atoms connecting them, can form a ring, at a temperature of from -60 to $200^\circ C$, at a pressure of from 0.5 to 100 bar, in solution, in suspension or in the gas phase, in the presence of a polymerization catalyst, wherein the polymerization catalyst prepared according to one or more of Claims 1 - 8 is used.
- 25 10. The process according to Claim 9, wherein ethylene or propylene is polymerized or copolymerized.
- 30
- 35
- 40
- 45
- 50
- 55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 10 7331

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 442 725 (MITSUI PETROCHEMICAL INDUSTRIES, LTD) * the whole document *	1-11	C08F10/00 C08F4/02 C08F4/642
Y	EP-A-0 368 644 (EXXON CHEMICAL PATENTS INC.) * the whole document *	1-11	
Y	EP-A-0 399 347 (HOECHST AKTIENGESELLSCHAFT) * page 7, line 27 - line 31 * -----	1-11	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C08F
Place of search THE HAGUE		Date of completion of the search 25 NOVEMBER 1992	Examiner KAUMANN E.K.-H.
CATEGORY OF CITED DOCUMENTS			
<p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>----- & : member of the same patent family, corresponding document</p>			